Detergent Composition and Water Quality

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It is a pleasure to speak to you tonight on the effects of components of detergents on the quality of our nation's waters. The problems caused by phosphorus in waterways, the role of phosphorus in detergents, the consequences of introducing substitutes for phosphorus in detergents, and the costs of removing phosphorus in municipal sewage by modern treatment plants are complicated by many factors. In the short time allowed me this evening, I can only present a very rapid overview of these four basic problem areas.

Phosphorus in Natural Waters

Let us start with an examination of some natural waters. Lakes, rivers, streams, and even oceans are living systems. They are born, proceed through childhood to maturity, become old, and finally die. This process occurs whether man is present or not. It is due to siltation of the waters by erosion of the drainage areas, rain-washed inflow of nutrients from the decay of vegetation on the slopes, and the growth and decay of aquatic plants in the water itself. The three stages in the life cycle of lakes and waterways are referred to as "oligotrophic" (from

the Greek *oligos*, few or little; and "*trophe*," nourishments); "mesotrophic" (from *mesos*, middle or intermediate); and "eutrophic" (from *eu*, good or well nourished). Without the intervention of man, the ageing process is very slow. It is estimated that Lake Erie would probably have attained its present state of eutrophication around the year 50,000 by natural processes. Similarly Lake Superior may not become eutrophic until the year 100,000 if not polluted by man.

Before one can proceed to improve the trophic state of a lake or stream, one must have a quantitative, objective method of measuring the current trophic level. Such a method is also needed to monitor the changes brought about by any treatment or control process. Water courses are often characterized by measuring chemical and biological parameters. Chemical analyses alone are not sufficient to establish the trophic level of watercourses. The results of biological analyses, however, are very significant and can be used as a trophic index. For example, oligotrophic waters may contain many species of organisms but only a few of each species. The system is well diversified and in balance. Eutrophic waters, on the other hand, generally contain few species but a very large number of each species. In most eutrophic waters, certain organisms usually referred to as algae predominate. Thus a study of the number and diversity of organisms present in a body of water is very

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helpful in assessing its trophic state. However, such studies are less useful to measure the short term changes that might result from the elimination of a nutrient or pollutant. Considerable time is required for a biological system to equilibrate. A rapid assay method is needed. The Pacific Northwest Water Research Laboratory of the Environmental Protection Agency was assigned the task of developing such a method. In cooperation with the detergent, chemical and food industries, the Tennessee Valley Authority and the U.S. Department of Agriculture, this laboratory developed an algal assay procedure[2] which can be carried out in three different ways: 1) in a flask, referred to as the "bottle test"; 2) in a continuous flow chemostat system; and 3) *in situ*. The simplest of the three is the "bottle test." Here one simply places a filtered sample of the water to be tested in a flask, adds a known inoculum of the test organism, exposes the flask to light of known constant intensity at a controlled temperature, counts the number of cells at prescribed time intervals, and plots a growth curve. The second method involves the use of a continuously flowing water system to which is added the test organism. The flow rate is adjusted until the number of cells per unit volume remains constant. This system gives a truer measure of growth rate, but is more time-consuming and expensive. The third method consists of immersing a large glass or plastic container into the lake or river of interest, adding the test organism to the water in the container, and allowing the organism to grow under the natural environmental conditions that prevail over the lake or river. Samples are taken out periodically and the number of cells counted. This procedure is the best approximation to the natural system but again is slower and much more expensive than the "bottle test." Thus we shall confine our discussion to the "bottle test." The organisms recommended for this test are: *Selenastrum capricornutum*, a nitrogen fixer; and *Micro-*

cystis aeruginosa, a non-nitrogen fixer. These organisms are grown under standard conditions to a preset number of cells per milliliter and are then used to inoculate waters under test.

In the fall of 1970, a program was initiated to conduct a series of algal assays on waters from nine Oregon lakes on a quarterly basis[3]. The objectives of the study were to 1) determine the effects of seasonal changes on the ability of the waters to support algal growth, 2) correlate the chemistry of the waters with their ability to support algal growth, and 3) evaluate the effects on algal growth of adding various nutrients to the waters. The assays were carried out in 500-ml Erlenmeyer flasks each containing 250 ml of water sample which had been filtered through a 0.45-micron filter to remove organisms naturally present in the water. Each flask was inoculated with a seven-day-old culture of *Selanastrum capricornutum*. The contents were incubated at $24\pm2°C$ for 21 days under continuous cool-white fluorescent lights producing an intensity of 400 foot-candles and shaken gently. The number and size of organisms were then measured by means of an electronic particle counter equipped with a "mean-cell volume" computer. The chemical compositions of the waters in the nine lakes are listed in Table 1 (see footnote 3). Upper Klamath Lake is obviously the most polluted and Waldo Lake the least. Let us see how their waters respond to inoculation with *Selenastrum capricornutum*. Table 2 (see footnote 3) contains the data from such studies. Note that water from Lakes Diamond and Triangle with the highest dissolved phosphorus concentration also show the greatest algal growth rate, whereas Upper Klamath Lake water with the highest dissolved inorganic carbon and dissolved nitrogen but intermediate dissolved phosphorus concentrations yielded intermediate *S. capricornutum*

[2]Algal Assay Procedure, Battle Test; National Eutrophication Research Program, Environmental Protection Agency, August 1971, Corvallis, Oregon 97330.

[3]Algal Responses to Nutrient Additions In Natural Waters: Laboratory Assays; Thomas E. Maloney, William E. Miller and Tamotsu Shiroyama; National Eutrophication Research Program, National Environmental Research Center, Environmental Protection Agency, Corvallis, Oregon 97330.

Table 1.—Chemical properties of filtered lake waters

Determination[1]	Lake								
	Woahink	Tahken-itch	Ten Mile	Lake of the Woods	Upper Klamath	Diamond	Odell	Waldo	Triangle
pH	6.7	7.0	7.0	7.1	7.7	7.0	6.9	6.1	7.2
Alkalinity (as $CaCO_3$)	9	16	21	14	54	22	17	2	14
NH_3-N	⟨0.010	0.100	⟨0.010	⟨0.010	0.350	0.290	0.020	⟨0.010	0.220
NO_3-N	0.024	0.066	0.004	0.014	0.038	0.032	0.010	0.010	0.012
Kjeldahl-N	0.400	0.500	0.500	1.000	1.200	0.800	0.300	0.100	0.700
Ortho-P	0.001	0.004	0.001	⟨0.001	0.017	0.038	0.026	0.001	0.040
Total Dissolved P	0.006	0.016	0.009	0.009	0.040	0.058	0.029	⟨0.005	0.063
Sol. inorganic C	1.0	3.0	5.0	3.0	13.0	5.0	4.0	⟨1.0	3.0
Sol. organic C	2.0	5.0	3.0	2.0	10.0	4.0	1.0	⟨1.0	2.0

[1] All chemical concentrations in mg/l.

growth rates. Fig. 1—9 (see footnote 3) show the effect on the algal growth rates when soluble nutrients containing nitrogen, phosphorus, and carbon are added to the lake waters. Note that 20 times as much nitrogen and 200 times as much carbon as phosphorus was added to produce the observed growth rates. In the case of Upper Klamath Lake water, it was already so rich in nutrients that further additions produced only a slight increase over the very high control growth rate. Nontheless, 200 times as much carbon as phosphorus was required to produce the same algal growth rate observed. Diamond and Triangle Lake waters also produced high growth rates without the addition of nutrients, and again, additions produced little or no effect. Waldo Lake water, on the other hand, was so deficient in all nutrients that additions of nitrogen, phosphorus, carbon, and even combinations of these nutrients produced a relatively small increase in the algal growth rate. Several additions would have been required to significantly affect the growth rate.

If one plots the algal growth rate in all the lake waters against the nitrogen content of the lake waters (fig. 10) (see footnote 3), there appears to be no correlation. A similar plot for growth rate versus soluble inorganic carbon (fig. 11) (see footnote 3), likewise shows no correlation. On the other hand, if the growth rates are plotted against the concentrations of phosphorus in the waters, the points fall essentially on a straight line (fig. 12) (see footnote 3). This plot is very strong

evidence that phosphorus is the algal growth rate controlling element in these nine lake waters. Studies on other water bodies have produced similar results in most cases. There are a few exceptions. Some lakes are so deficient in carbon and nitrogen nutrients that these two elements appear to be the growth-controlling substances. Some marine waters tend to show this behavior. By and large though, the algal growth rate is proportional to the phosphorus concentration. Thus, the input of phosphorus into our waters should be carefully limited. True, it cannot be eliminated entirely, but reducing the phosphorus content of many waters by even 50% will cut the algal growth rate in two. In waters where the phosphorus content is close to the critical eutrophic level reducing the phosphorus input by a factor of two may protect the lake from algal blooms indefinitely. Of course, there are differences of opinion as to how this reduction is to be achieved. As detergents account for about 60% of the phosphorus in municipal sewage, some advocate complete elimination of all forms of phosphorus from detergent formulations. Others point out the problems associated with the use of some phosphorus-free substitutes and strongly recommend removal of the phosphorus compounds at the municipal sewage treatment plant rather than banning them from detergent formulations. A look at the role of phosphorus in detergents and at the costs of removing phosphorus from municipal sewage may shed some light on this controversy.

Phosphorus in Detergents
The Detergent Process

A detergent must accomplish three basic actions to effectively wash clothing or clean any substance: 1) it must preferentially wet the substrate, in this case the cloth, be it cotton or synthetic fiber, so that the soil is lifted off the substrate; 2) once the soil has been released from the substrate, the detergent solution must either dissolve the soil or keep it in suspension in such a manner that it is not redeposited on the fabric; and 3) it must remove the ions which would interfere with this suspension process. These ions are responsible for the "hardness" of the water and usually consist of calcium, magnesium and iron in the ferric state. Thus, a detergent formulation must include at least three constituents: 1) a surfactant to "wet" the fabric and the soil particles; 2) a protective colloid, to coat the soil particles with a very thin film to prevent their coalescing into large clumps which would then deposit on the fabric; and 3) a precipitant or sequestering agent, to either precipitate the undesirable "hard" ions or bind them into uncharged complexes which can no longer interfere with the soil suspension process.

Precipitating Detergents

Soap—For years soap was used to accomplish all three functions. However, soap is successful only to a limited extent for the following reasons. Soap is made by the reaction of animal and vegetable fats with lye (sodium hydroxide) or for special soaps, potash. Thus soap is the sodium or potassium salt of stearic, palmitic, or oleic acids, depending upon the fat used (beef fat or oils such as palm, olive, corn, or cottonseed). When soap is "dissolved" in water, it does not really dissolve. Most of the soap remains suspended in the water in groups of molecules known as micelles. The suspended soap is capable of wetting both the fabric and many soil particles, thereby removing the soil from the fabric and suspending it within the micelles. A small amount of soap does dissolve. The dissolved soap dissociates into sodium or potassium ions and ions of the
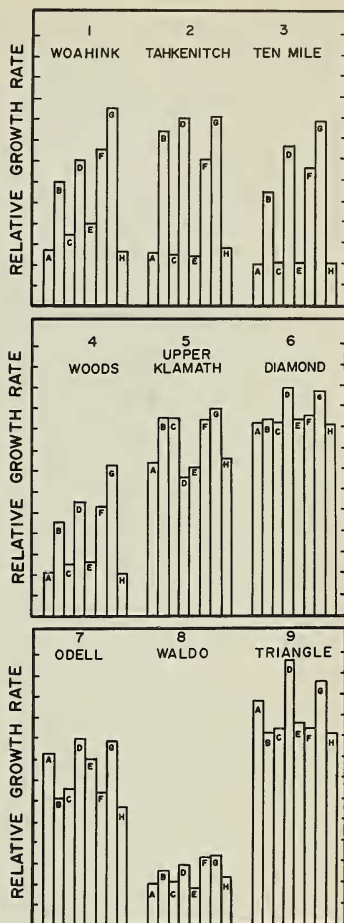

Fig. 1-9.—Effect of various nutrient additions to lake waters on the growth rate of *S. capricornutum*. A = 1.0 mg nitrogen/l; B = 0.05 mg phosphorus/l; C = 10.0 mg carbon/l; D = 1.0 mg nitrogen + 0.05 mg phosphorus/l; E = 1.0 mg nitrogen + 10.0 mg carbon/l; F = 0.05 mg phosphorus + 10.0 mg carbon/l; G = 1.0 mg nitrogen + 0.05 mg phosphorus + 10.0 mg carbon/l; and H = control (no nutrient added).

Table 2.—Comparison of average daily growth rates of *S. capricornutum* with dissolved nitrogen and phosphorus concentrations in lake waters.

Lake	Ave. Algal Growth Rate	Dissolved P mg/1	Dissolved N[1] mg/1
Woahink	0.23	0.006	0.034
Tahkenitch	0.28	0.016	0.166
Ten Mile	0.21	0.009	0.104
Lake of the Woods	0.21	0.009	0.204
Upper Klamath	0.76	0.040	0.388
Diamond	0.92	0.058	0.322
Odell	0.58	0.029	0.030
Waldo	0.23	< 0.005	0.020
Triangle	0.92	0.063	0.232

[1] NH_3-N+NO_3-N

fatty acid characteristic of the fat from which the soap had been made. Some of the fatty acid ions combine with the hydrogen ions in the water to form undissociated fatty acid molecules which remain suspended in the water. The remaining hydroxyl ions enhance the process of soil suspension as they are negatively charged and tend to stabilize the colloid formed. The hydroxyl ions also convert some soil substances to forms which are more soluble in water. Thus soap appears to be a reasonably effective cleaning agent. Unfortunately, calcium, magnesium, and iron ions, commonly found in hard waters, form insoluble salts with fatty acid ions. These salts precipitate as a scum of varying hardness depending upon the fatty acid used to make the soap; salts of stearic acid are the hardest and those of the oleic acids are the softest (hard and soft as used here refer to their tactile (feel) properties and not to their chemical properties as when speaking of water hardness).
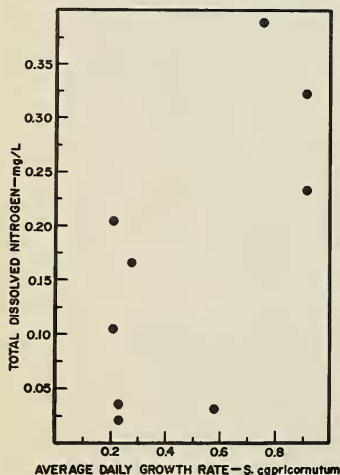

Fig. 10.—Effect of the concentration of total dissolved nitrogen on the growth rate of *S. capricornutum*.
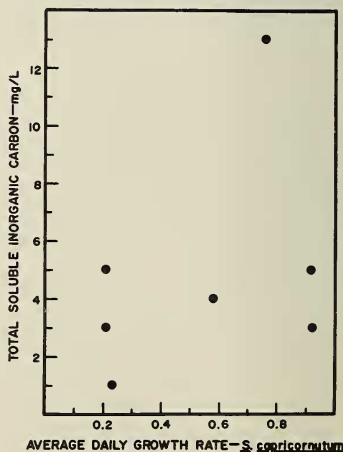

Fig. 11.—Effect of the concentration of total soluble inorganic carbon on the growth rate of *S. capricornutum*.
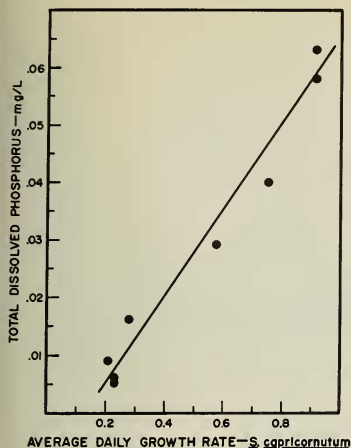
Fig. 12.—Effect of the concentration of total dissolved phosphorus on the growth rate of *S. capricornutum*.

Scum formation not only uses up soap, requiring more soap for effective cleaning, but also has a tendency to deposit a sticky layer on clothing and laundry equipment. This layer attracts and holds other dirt on fabric surfaces thereby imparting the characteristic "tattle-tale gray" to clothing after a dozen or so washings. On laundry equipment, the deposits interfere with proper functioning of machine items with close tolerances (pumps and valves) thereby increasing service frequency. Fig. 13 contains a table of commonly used fats, the corresponding fatty acids, melting point of the fatty acids, a typical saponification reaction using beef fat and lye, and the ionization and combination reactions of dissolved soap. As shown in the figure, soap consists of a long, water insoluble tail and a short water-soluble head. The long, water insoluble, organic tail can wet and stick to many dirt surfaces which are not wet by water. As the water-soluble head of the soap molecule has a strong affinity for water, dirt particles wet by the organic tail are removed from the fabric or other articles and suspended in the water. This process is illustrated schematically in fig. 14. Laboratory studies showed that the more soluble the head of the molecule was in water and the more soluble the tail in organic substances, the more powerful the surfactant. This observation served as the basis for the synthesis of the very effective surfactants used in modern detergents.
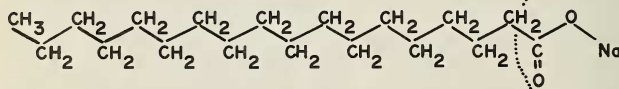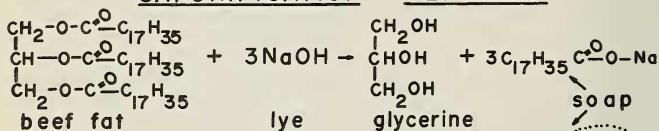
Washing Soda Formulations.—From the above discussion, it is obvious that the prevention of scum formation is highly desirable. Thus some soap makers included sodium carbonate (washing soda) into their mix when pressing the bars. The sodium carbonate in these soaps precipitated the calcium, magnesium and iron as insoluble, powdery salts thereby reducing the tendency to form sticky scums. As the fatty acids competed with the carbonate for the "hardness" ions, some scum still formed. The marketing of washing soda in a separate box was tried. The user was advised to add the soda to the wash water before adding the soap. This precipitated the hardness ions in the desired fine, powdery, non-adhering form without interference by the soap. To some extent, this was reasonably successful. However, some of the precipitated material still deposited on the fabric and machine parts as the water level dropped during the wash-water discharge cycle.

With the discovery of synthetic surfactants (wetting agents) in 1930, combinations of surfactant and sodium carbonate were marketed. These were more successful than the soap/carbonate mixtures as they did not contain fatty acids to form sticky residues. Nonetheless, some of the precipitated calcium, magnesium and iron carbonates did adhere to the fabrics giving the material a harsh feel. When the water contained iron salts, the precipitate was particularly undesirable as it imparted a yellow color to white items in the wash. To minimize these effects, antiredeposition agents (carboxymethylcellulose), blueing, and even bleaches were added to the products marketed in the twenty-year period from 1930 to 1950.

In 1970, sodium carbonate-based formulations reappeared on the consumer market.

FAT	PRINCIPAL FATTY ACID	EMPIRICAL FORMULA	M.P. °C
beef fat	stearic	$C_{17}H_{35}C\overset{O}{-}OH$	69-70
palm oil	palmitic	$C_{15}H_{31}C\overset{O}{-}OH$	63-64
olive oil	oleic	$C_{17}H_{33}C\overset{O}{-}OH$	14
cotton seed	linoleic	$C_{17}H_{31}C\overset{O}{-}OH$	~ -18

SAPONIFICATION REACTION

$$
\begin{matrix}
CH_2-O-C\overset{O}{-}C_{17}H_{35} \\
CH-O-C\overset{O}{-}C_{17}H_{35} \\
CH_2-O-C\overset{O}{-}C_{17}H_{35}
\end{matrix}
+ 3NaOH \rightarrow
\begin{matrix}
CH_2OH \\
CHOH \\
CH_2OH
\end{matrix}
+ 3C_{17}H_{35}C\overset{O}{-}O-Na
$$

beef fat   lye   glycerine   soap

water insoluble, organic tail

water soluble head

Reactions of Soap with Water and Hardness Ions

$$C_{17}H_{35}C\overset{O}{-}O-Na + H_2O \rightarrow C_{17}H_{35}C\overset{O}{-}O-H + Na^+ + OH^-$$

free fatty acid

$$\xrightarrow{\text{in water}} [C_{17}H_{35}C\overset{O}{-}O-]^- + Na^+$$

stearate ion

$$2[C_{17}H_{35}C\overset{O}{-}O-]^- + Ca^{++} \rightarrow (C_{17}H_{35}C\overset{O}{-}O-)_2 Ca$$

hardness ion
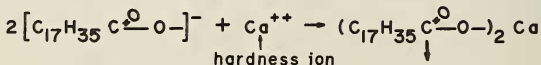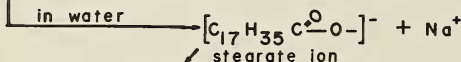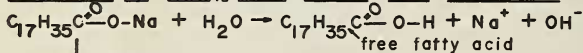
soap scum
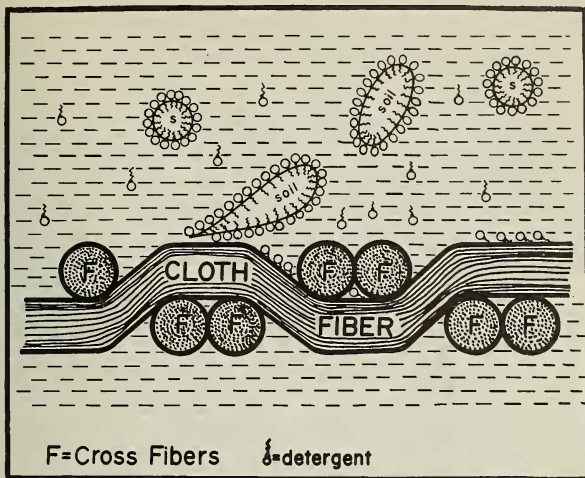
Fig. 13.—Soap and its reactions.

Fig. 14.—The removal of organic soil from a cloth fiber.

Current formulations may include from 50-85% sodium carbonate, about 6% modified sodium silicate $(Na_2O.2SiO_2)$, 20 to 10% surfactant (usually of the non-ionic type), about 1% carboxymethylcellulose and the rest optical brighteners and fillers. The pH of solutions of these formulations is about 10.5. This value is higher than that of solutions of soap (about 9) or the formulations which will be discussed later. As pointed out above, these formulations depend upon the precipitation of calcium, magnesium, and iron ions as insoluble carbonates, thereby softening the water. The surfactant then releases the soil from the fabric. The carboxymethylcellulose prevents the redeposition of the soil and, to some extent, of the precipitated carbonates. Although one manufacturer claims that no problems are encountered by users of his product, regardless of water hardness, our research indicates there is a definite buildup of inorganic solids in fabrics washed with these materials. Buildup of inorganics is referred to as "ash buildup" because of the manner in which the inorganics are determined analytically. The cloth is slowly charred in a crucible, the crucible is then heated to a dull red heat, cooled and weighed. High inorganic salt content not only imparts a coarse feel to the fabric but also decreases its wear resistance. Of course, in high-iron areas, white items will appear yellowish after a few washings just as with the earlier formulations. Furthermore, private information suggests that at least one large home washer manufacturer is experiencing interference with proper functioning of his washers when carbonate-based formualtions are used.

Borax.—The compound borax (sodium tetraborate decahydrate) has been marketed as a cleaning agent with no additives for many years. Its cleaning power is due to the alkalinity developed when the compound is hydrolyzed by water and also on the formation of insoluble borates with the "hardness" ions previously discussed. Borax never enjoyed wide acceptance as a household laundry detergent but has maintained consistent, though small, sales as a hard-surface cleaner.

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Recently, a formulation containing 30% sodium perborate ($NaBO_3 \cdot H_2O$) has been introduced as a phosphate-free detergent. However, most formulations which include perborates use only about 2% to impart mild bleaching action. This occurs only at high water temperatures. As the water temperature used by American home washers is generally about 135°F, very little if any bleaching takes place. The product has been more or less successful in Europe where 180°F water is used. Humans are very tolerant to borates. About 10 to 20 mg may be ingested daily in food with no apparent ill effects.

The U.S. Public Health Service recommends that drinking water contain not more than 1 mg of boron per liter of water, but western U.S. waters may contain 5-15 mg/liter. However, because of its phytotoxicity (0.5 to 1.0 mg/liter damaging sensitive plants), boron containing formulations should not be encouraged.

Surfactant/Soap Combinations.—There are a number of liquid, all-purpose cleaners which consist of 80% saponified vegetable oils, 10-15% surfactant of the non-ionic type, a few percent of an organic solvent such as butylcellosolve, sometimes free ammonia, and an optical brightener. These perform satisfactorily as general purpose, hard-surface cleaners. Their performance in the household-type washer is being checked. One formulation consists of about 80% saponified vegetable oil, 15% ethoxylated alcohols, assorted impurities, and 0.1% optical brightener. Its manufacturer claims it to be completely biodegradable and it well may be. How well it washes is unknown at this time. Scum formation may be a problem.

Non-Precipitating Detergents

Water Softeners.—It is now clear that for the best washing efficiency, one must either remove the interfering "hardness" ions by a completely separate operation, not in the presence of soap, or render these ions inactive by binding them into neutral complexes which are very soluble, do not precipitate out, and are discharged with the wash water. The first alternative may be accomplished by installing a water softener for the entire household, or more economically by attaching a small water softener to the wash water intake of the home washer. One machine manufacturer did develop such a device about 15 years ago. It consisted of a cylinder about 18" long and 5" in diameter filled with conventional water softening zeolites which could be regenerated by adding a pound of salt to the cylinder. About 6 months wash use between regenerations, for the average family, was claimed. The item never reached the consumer market because of the advent of the highly efficient, chelating (sequestering) detergent which obviated its need. Today synthetic ion-exchange resins in replaceable or regenerable cartridges could be readily attached to the home washer at very reasonable cost. Information from the home laundry industry indicates that the device is being reconsidered by machine manufacturers.

Sequestering Formulations.—In 1946 the discovery that sodium tripolyphosphate (STPP) was able to bind the hardness ions into soluble, noninterfering complexes revolutionized the detergent industry. Within the next decade, practically all of the formulations intended for heavy duty use contained from 25 to 50% STPP by weight; presoaks contained as much as 70-80% STPP. They also contained enzymes. However, enzymes are a completely separate problem so they will not be discussed in this paper.

Sodium Tripolyphosphate (STPP).—Having discussed the functions of a detergent, we are now in a position to appreciate the composition of a modern, high efficiency detergent given below:

Each item in this formulation was included after extensive research and testing. Therefore, the deletion of any one would result in some reduction in the performance of the product. Substitutes should be carefully considered before changes are made lest the cure be worse than the disease.

From a performance standpoint, STPP appears to be the ideal builder. It is capable of sequestering the "hardness" ions into soluble, neutral complexes; it is mild, pH of solutions of formulations are about 9.9; and

Typical Heavy-Duty Granular, Detergent Formulation

Material	Percent by wt.	Purpose
sodium dodecylbenzene sulfonate	18.0	surfactant
sodium xylene sulfonate	3.0	antidusting agent
dethanolamide of coconut fatty acids	3.0	foam booster
sodium tripolyphosphate	50.0	builder (sequestrant)
sodium silicate	6.0	anticorrosion agent
carboxymethylcellulose	0.5	soil redeposition preventive
optical brightener[a]	0.3	fluorescent whitener
benzotriazole	0.1	antitarnishing agent
other inorganic salts and water	19.1	fillers (usually sodium sulfate)

[a] This is usually a 50/50 mixture of a fluorescent dye which attaches itself to cotton and a fluorescent dye which combines with synthetic fibers. Typical examples are bis stilbenedisulfonate and triazolylstilbene-sulfonate.

it possesses sufficient reserve alkalinity to saponify (convert to soluble salts) oily soil removed from clothing. Furthermore, sodium tripolyphosphate readily hydrolyzes into sodium orthophosphate which has no appreciable sequestering power, thereby releasing the metal ions previously solubilized. These ions combine with the orthophosphate ions to form insoluble salts which then precipitate out. Thus the hardness ions are held in solution during the washing process but are released to precipitate out later either during the sewage treatment process or in septic tank drain fields. It is interesting to note that the phosphates of heavy metals such as mercury, cadmium, and lead are also only slightly soluble. Thus the presence of orthophosphate ions in water tends to limit the concentration of these toxic metal ions to values frequently less than one part per million. The exact value will depend upon the pH of the water and upon the dissolved oxygen content, that is, whether the system is predominatly in an oxidized or a reduced state.

Unfortunately, as discussed above, orthophosphate ions have been identified as contributing to accelerating the growth of undesirable algal species, thereby contributing to the premature aging of watercourses. Legislation limiting the amount of STPP, or any other phosphate, in detergents has been enacted by some communities; others are planning to ban the use of all phosphates in

detergent products sold within their jurisdiction.

The furor about the use of phosphates has led to the appearance of many phosphate-free formulations with varying degrees of washing efficacy. Most formulations are rehashes of the precipitating detergent formulas discussed in the earlier parts of this paper. A few detergent manufacturers substituted some other sequestering agent for STPP. Some of the sequestrants used were:

NTA (nitrilotriacetic acid).—Until very recently, NTA appeared to be the most promising sequestering substitute for STPP. However, serious questions as to its teratogenicity have been raised by the early work by the Public Health Service. The soap and detergent industry is voluntarily withholding this compound until further studies prove or disprove the existence of the hazards suggested.

EDTA (ethylenediamine tetracetic acid).—EDTA has been known to be a very effective chelating agent (sequestrant) long before NTA. However, it was also known to biodegrade very slowly so its use in household detergents was not pushed by the industry. It has been and is used to a very limited extent in special purpose cleaners.

Sodium Citrate.—The citrates should be ideal substitutes as they biodegrade readily, are not toxic, and can be prepared in large quantities at reasonable cost. Unfortunately,

citrates are only good chelators at high pH values—about 12. Products with such a high pH would not meet product safety standards. Recent research indicates that citrates are effective at lower pH values if special surfactants are used. Several new formulations are being evaluated.

SODA (disodium oxydiacetate).—SODA is a new compound which has chelating properties midway between STPP and NTA. It is said to biodegrade readily with practically no acclimitization period. As it does not contain phosphorus, nitrogen, or potassium, biostimulatory effects would not be anticipated. Being weaker in chelating power than NTA, it may not transfer metals across the placental barrier and into the fetus as appears to be the case with NTA. However, no experimental information is available on this point. SODA can be prepared cheaply and in the amounts required as the raw materials are formaldehyde, carbon monoxide and water. At this time, all that can be said is that the compound is "of interest."

Pollution Potential vs. Detergent Type

A simple way of estimating the amounts of components of a detergent formulation which would be added to receiving waters if that particular formulation were adopted by all users is to compute the amount of phosphorus presently contributed by detergents and compute the equivalent amount of detergent formulation involved. Then assume that the same weight of any other formulation would be used. From the percent composition of the formulation, the amount of a particular component can be readily calculated. This method is superior to determining the total sales of detergent products and using that figure as a base because the amount used by owners of septic tank systems is difficult to determine and most of the discharge from these systems remains in the ground. Furthermore, the computation method given below will furnish data on the upper limit of resulting concentrations without requiring extensive rainfall or river flow data. It is understood that the computed values are estimates which may be in error by 50% (that is, may be higher or lower by

½ of the value assigned) but nonetheless they are useful estimates. The procedure is as follows:

A. *Assumptions:*

1. 60% of the elemental phosphorus in municipal sewage effluent is contributed by detergents; the other 40% is probably from human excreta, discarded food products, discharges from various process industries, etc.

2. 15% of the elemental phosphorus entering a municipal sewage treatment plant is removed, in the activated sludge or trickling filter, etc. Thus we may assume a 15% phosphorus loss in passing through the plant.

3. The average detergent contains 40% by weight, STPP. Until very recently, this has been a representative value. During the last few months, manufacturers have attempted to reduce the STPP content, but for the purposes of our calculations 40% is valid.

4. The increment of phosphate from tap water to secondary effluent is 25 mg/liter. This value is based on the fact that municipal drinking water has a practically zero phosphate content, whereas, secondary effluent contains 25 mg/liter phosphate. The 25 mg/liter phosphate content of the municipal sewage effluent must represent the increase through one water-use cycle. The equivalent amount of elemental phosphorus is 8.3 mg/liter.

B. *Calculations:*

1. If 15% is removed during treatment, the true P increment per use is $8.3 \times 100/85 = 9.8$ mg/liter, or approximately 10 mg/liter.

2. However, only 60% is from detergents, so .6 x 10 = 6 mg/liter of P is from detergents.

3. This corresponds to $6 \times 3.95 = 23.7$ mg/liter of STPP.

4. The corresponding concentration of the total detergent formulation is $23.7 \times 100/40 = 59.3$ mg/liter.

5. To simplify calculations, it is a justifiable assumption that 60 mg/liter be used instead of 59.3. Thus, regardless of the composition of the detergent, the total dissolved solids (TDS) increment would be 60 mg/liter. This is about 10% of the average TDS present in effluents.

6. Suppose a carbonate-based, non-chelating detergent completely replaced phosphate-based detergents and it contained 40%, by weight, sodium carbonate and 10% modified sodium silicate, $Na_2O.2SiO_2$. The carbonate, silicate, and sodium ions added to the effluent would be:

a. amount of Na_2CO_3 would be $40/100 \times 60 = 24$ mg/liter, and the corresponding $CO_3^= = 24 \times CO_3^=/Na_2CO_3 = 24 \times 60/106 = 13.6$ mg/liter. If acidified this would generate about 14 mg/liter of bicarbonate, an increase of less than 5% of the

amount now present in sewage effluent. Thus, insofar as bicarbonate formation may be of concern, even complete substitution does not appear to constitute a threat to the aquatic environment. The addition of 14 mg/liter of carbonates to the 310 already present can hardly be critical. Formulations containing 60% sodium carbonate would add 1.5 times the amounts calculated above. These amounts still do not appear to be cause for alarm.

b. The amount of modified sodium silicate introduced would be 6 mg. The corresponding amount of silicate is $6 \times 152/182 = 5$ mg, or about 10% of the amount already present in sewage effluent. Here again, it is difficult to foresee how this increase could be deleterious but firm data is lacking.

c. The sodium ion introduced by both the sodium carbonate and modified silicate is $24 \times 46/106 = 10.4$ mg/liter (from the carbonate) and 6 $\times 46/182 = 1.5$ mg/liter (from the silicate), giving a total of 11.9 or 12 mg/liter. This again is about 10% of the amount already present. In judging the effects of carbonate/silicate formulations, it should be remembered that many current phosphate formulations contain 6% silicate, so at the most the change from the amount of sodium ions now being introduced, due to the increased silicate content, would be half the amount calculated above, i.e., $1.5 \times 1/2 = 0.8$ mg/liter of Na^+. As 23.7 mg of STPP contribute 7.3 mg/liter of sodium ions, the Na^+ contribution by the sodium carbonate formulations is only 3.9 mg/liter greater than that introduced by STPP formulations. This is about 3% of the amount now present in municipal sewage effluent.

7. Calculations for sulphate will not be discussed in detail as the amount of sodium sulphate used in the phosphate-free formulations is usually about the same as in the STPP-based detergents now in use. At the most a 4% increase could be anticipated; this is unlikely.

8. Assuming the new 30% sodium perborate formulation completely replaced the STPP detergents, the amount of boron discharged to our waterways would be $30/100 \times 60 \times B/NaBO_2.H_2O = 30/100 \times 60 \times 11/100 = $ about 2 mg/liter. Although one could drink water of this boron content without harm, the water would be unsuitable for irrigation purposes. As mentioned before, boron at the 0.5-1.0 mg/liter level damages sensitive plants; 4 mg/liter damages all plants. Thus, if boron containing detergents captured 25% of the market, an environmental problem might result. This could be particularly acute in areas where effluents are used downstream or directly for crop irrigation or in areas where septic tanks were used extensively. The accumulation of boron in the drain fields would soon render the area unsuitable for any plant life. On the other hand, fish seem to be very tolerant to boron compounds; i.e., 96 hour TL_{50} values in excess of 3000 mg/liter have been recorded.

9. Since surfactant/liquid soap formulations are said to be completely biodegradable, the problem seems to be one of biochemical oxygen demand load on the rivers and streams. This load should be no greater than if ordinary soap were used. There is good reason to believe that the components of these detergents would degrade at about the same rate as other biodegradable organics in municipal sewage. Thus the load would be on the treatment plant; a properly operating plant would discharge no more than at present. Septic tank systems should also be able to degrade these materials as effectively as materials now in use. The performance of liquid soap formulations in the home laundry remains to be established.

10. NTA is a more effective chelating agent than STPP. On a weight basis, 1 gram of NTA will chelate as much calcium or magnesium as 1.4 grams of STPP. Thus a formulation using 40 wt % of STPP will require 40/1.4 or 28.6 wt % NTA. This corresponds to 17.2 grams of NTA if 60 grams of formulation are used as assumed above. The nitrogen added will be $17.2 \times N/NTA = 17.2 \times 14/257 = $ about 1 mg/liter. This is only about 3% of the total nitrogen currently present in waste waters. It is difficult to see how this small increment could generate environmental problems. Unfortunately, NTA is a powerful chelating agent. Experiments suggest that cadmium chelates of NTA may be transported across the placental barrier with consequent damage to the fetus. Use of NTA has been voluntarily withheld by the detergent soap industry until additional experiments are completed.

11. On a weight basis, SODA (disodium oxydiacetete) is said to be 1.4 times as effective as NTA and 2.1 times as efficient as STPP. In addition, SODA is said to biodegrade without acclimatization; if so, it may impose no discernible environmental load. Its chelates are said to be intermediate in stability to those of NTA and STPP. Thus, heavy metal chelates may not be transported past the placental barrier. On the basis of very preliminary information, SODA appears to have some promise as a substitute builder. Considerable research on its degradation mechanism and the toxicity of intermediate degradation products remains to be done.
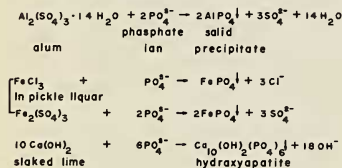
Costs of Phosphorus Removal from Sewage

The sewage treatment process used by various cities and municipalities may consist of a simple sedimentation basin to remove suspended solids or an elaborate series of sedimentation basins, activated sludge aeration tanks to microbiologically degrade dissolved organics in the sewage, adsorption towers to remove organics that resist microbiological degradation, and finally chlorination to destroy bacteria and viruses before

the sewage is discharged to the receiving waters.

Phosphorus may be removed from the sewage microbiologically. By carefully controlling the concentration of nutrients (raw sewage) fed to the activated sludge tanks the bacteria are made to "take-up" the maximum amount of phosphorus. However, even under optimum conditions, the maximum phosphorus removal achieved by this technique is about 80%. As it is difficult to maintain optimum conditions continuously, only 15-20% phosphorus removal is attained by most treatment plants. The simplest and most effective method of removing phosphorus from sewage is by the use of chemical precipitants after the activated sludge treatment. The chemicals used and their reactions with phosphate ions are given in Table 3. The particular chemical selected

TABLE 3
Removal of Phosphate by Chemicals

$$Al_2(SO_4)_3 \cdot 14\,H_2O + 2\,PO_4^{3-} \rightarrow 2\,AlPO_4 + 3\,SO_4^{2-} + 14\,H_2O$$

alum   phosphate   solid
ion   precipitate

$$\begin{bmatrix} FeCl_3 \\ in\ pickle\ liquor \\ Fe_2(SO_4)_3 \end{bmatrix}$$

$$FeCl_3 + PO_4^{3-} \rightarrow FePO_4 + 3\,Cl^-$$

$$Fe_2(SO_4)_3 + 2\,PO_4^{3-} \rightarrow 2\,FePO_4 + 3\,SO_4^{2-}$$

$$10\,Ca(OH)_2 + 6\,PO_4^{3-} \rightarrow Ca_{10}(OH)_2(PO_4)_6 + 18\,OH^-$$

slaked lime   hydroxyapatite

will, of course, depend upon the location of the treatment plant and the price of the chemicals delivered to the plant. For example, a plant located close to a steel processing mill will find it advantageous to use "pickle liquor" which is rich in ferric ion and is a waste product the steel mill is anxious to dispose of. On the other hand, a plant located close to a bauxite mine might find it most economical to use an aluminum salt as a precipitant. As lime is available everywhere at low cost, it is the most universally used chemical precipitant. However, all three metallic ions (aluminum, ferric, and calcium) may be used at reasonable cost at all locations. Whereas the cost to treat 1000 gallons of sewage decreases as the plant size increases, the cost for the chemicals used is relatively constant, except for the small advantage of large quantity purchasing. The

values listed in Table 4 are based on a phosphorus concentration of 10 mg/liter in the influent sewage, 80% removal, and the assumption that all chemicals are purchased at average delivered prices.

Of course, there are additional costs. Chemical storage tanks, feeders, and mixers must be installed. The additional sludge formed by the chemical precipitants must be handled and disposed of. Additional power and labor will be required. Taking all these factors into consideration, some representative cost figures are listed in Table 5. The costs are very reasonable. Perhaps removal at the treatment plant may be the solution to the phosphorus in detergents dilemma.

TABLE 4
Cost of Phosphorus Removal[a]
(in cents per thousand gallons,80% removal)

Plant Size mgd[1]	Chemical Cost	Cost Including Amortization of Treatment Equipment[b]
1	1.4	16
10	1.4	9
100	1.4	6

[1]million gallons per day.   [b]does not include costs for chemical storage tanks and sludge handling equipment.
[a]more detailed cost data in reference 3.

TABLE 5
Cost of Phosphorus Removal[a]   4

Average Total % P Removed	Cost in Dollars/Year/Capita[b]
80	2.50
90	4.00
98	5.00

[1]100 mgd plant.   [b]120 gallons of water per capita per day.
[a]more detailed cost data in reference 3.

May I conclude with a few words in reply to the claims that the detergent industry is over-selling detergents by recommending the use of more than is necessary. Figure 15 is a plot of the amount of STPP required to sequester varying amounts of calcium ions in water and the calcium ions in the soil of the wash load. (It is assumed that all the hardness is present in the form of calcium ions; magnesium and iron ions would show a similar relationship.) It is obvious that 1 cup of detergent product is insufficient for waters containing more than about 60 mg/

[4]Process Design Manual for Phosphorus Removal, U.S. Environmental Protection Agency, Technology Transfer Program No. 17010 GNP, Contract No. 14-12-936, October 1971.
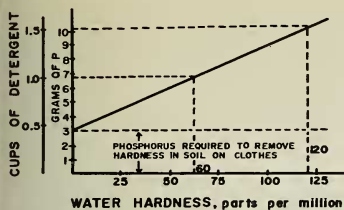
Fig. 15.—Phosphorus and detergent required to bind the hardness in water and soil, assuming a detergent product containing 35% sodium tripolyphosphate and a 17-gal capacity household washing machine.

liter (60 parts per million) of hardness ions. Approximately 90% of the U.S. population is using water containing more than this amount of hardness. As an example, the drinking water distributed to consumers in the District of Columbia contains, on the average, about 120 ppm of hardness ions. Assuming the household wash load is soiled with particulate matter equivalent to 3 grams of phosphorus, about 10.25 grams of phosphorus or 1½ cups of detergent formulation per wash load (using a top loading household washing machine) would be required. Of course, not all clothing is soiled to this extent. For example, ladies garments frequently are soiled with only a small amount of perspiration. But even in this case, 1 cup of detergent is required to sequester the hardness ions in the water if District of Columbia water is used. Thus, "experts" who claim that it is possible to wash clothes with small quantities of detergents (1/2 to 1/10 cup) either are unaware of the basic principles of chemical stoichiometry or are deliberately misrepresenting the facts, to the detriment of the public.

Summary

1. At the present state of the art, sequestering detergent formulations appear to be superior to precipitating formulations in laundering performance.

2. No environmentally acceptable, effective sequestrants have been positively identified to date. Sodium citrate would be an environmentally acceptable sequestrant if it could be used at lower pH values, e.g. 10 to 10.5. Research to develop suitable surfactants to produce effective washing formulations incorporating sodium citrate as the builder is in progress. A new compound, disodium oxydiacetate (SODA) has been announced as possibly meeting the requirements of being a nonpollutant and a satisfactory sequestrant. Little is known about its degradation mechanism, degradation end products, and the membrane transport characteristics of its chelates.

3. Some phosphate-free detergent formulations containing sodium carbonate and modified sodium silicate as builders have appeared on the market. Tests indicate at least one is not as effective as phosphates in its ability to remove soil form permanent press or synthetic fiber fabrics. However, preliminary calculations revealed no detrimental impact on the environment. Further research may improve the washing performance of such formulations.

4. An interim solution to the detergent problem may be to limit the amount of phosphorus compounds in detergents to that required to sequester 120 ppm hardness in water. This will accommodate the residents of 71 of the 100 largest cities of the United States which account for 25% of the total population of the U.S. (This does not mean that 75% of the people use water harder than 120 ppm. It simply indicates a lack of data for the very small municipalities and the individual well supplies.) The amount of STPP required to sequester 120 ppm hardness corresponds to about 7.25 grams phosphorus per wash load.. (This value does not include the phosphorus required to sequester the hardness in the soil.) Users in other areas could use proportionate amounts of formulation. An alternative might be to publish "hardness values" for different areas of the country and to package the phosphate separately. Each user would add the phosphate required to sequester the hardness in the water and the soil in the clothing, as indicated by the published values. (Soil values would be simply light, medium, and heavy and correspond to 1, 2, and 3 grams of phosphorus, respectively.)

5. Phosphorus may be removed to any desired degree by most treatment plants at nominal cost, averaging about $5.00 per year per capita. Thus removal at the treatment plant may prove to be the ultimate solution to the problem of eutrophication of the nation's waters by phosphorus.

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